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Humic substances (HS) were extracted from faecal “pellets” - ovoid phosphatic grains 50-200 µm in size - collected from commercially mined phosphatic sediments, in the Gafsa Basin. The phosphatic constituents were characterized by C, H, O, N, and S elemental analysis, Rock-Eval VI pyrolysis, Fourier-transformed infrared spectroscopy (FTIR) and solid state ^{13}C CPMAS NMR.

Humic (HA) and fulvic acids (FA) were isolated utilizing the standard method recommended by the International Humic Substances Society (IHSS). Their amounts were obtained by quantifying carbon in each fraction and in each step of the fractionation procedure. The total amount of HS carbon exceeds 75 % of the total organic carbon contained in the phosphatic grains, with a predominance of HA (about 70 %). These high contents of HS are well correlated with the total phosphorus content (P_2O_5 > 30 %) of the studied grains. Such high concentrations of HS in Eocene phosphatic sediments imply an excellent preservation of the organic matter within the pellets, both from a qualitative and quantitative point of view.

The elemental composition of HA and FA shows that both these fractions have rather low ash contents (7 % for HA, 13 % in FA) and distinctive elemental compositions. The C content increases from FA (55%) to HA (65 %), the H content being poorly variable between both fractions (ca.7 %). In contrast, the O content (13% in HA to 29 % in FA) decreases with increasing C content. Nitrogen and sulphur contents range respectively from 2 to 4 % and 5 to 13 % for HA and FA, respectively. The atomic ratios O/C and H/C values of 0.15 and 1.29 % in HA and 0.40 and 1.55% in FA, respectively, indicate that these humic compounds originated from marine aliphatic organic matter and only reached a low degree of thermal maturity.

The FTIR analysis of humic materials shows a striking predominance of aliphatic structures and O-containing functional groups over aromatic and condensed moieties. The

spectra obtained for HAs fractions show that HAs contain more aliphatic and aromatic structures than FAs, which are relatively richer in carboxylic groups and carbohydrates.

The structure of HAs and FAs was also investigated using solid state ^{13}C CPMAS NMR (Fig. 1). The displayed spectrum shows a strong aliphatic carbon peak (0-50 ppm), aliphatic carbon bound to oxygenated functions (50-110 ppm), aromatic carbon (100-160 ppm) and, finally, carboxylic/carbonyl functions (160-220 ppm). The ^{13}C NMR spectroscopic analysis is therefore consistent with the elementary and IRTF data, all indicating abundant oxygen-bearing aliphatic structures.

The study of the HS with Rock-Eval VI pyrolysis confirms the marine planktonic rigin of the organic matter located within phosphatic pellets as already stated by Belayouni and Trichet (1983). RE Pyrolysis also provides HI, OI and Tmax values confirming the humic character of the organic matter contained in pellets, i.e. that of an immature material.

Thus, all the analytical data obtained on these HA and FA witness the surprisingly good preservation of this sedimentary organic matter, in Eocene series (i.e. 50 Ma old). This good preservation resulted from the conjunction of several processes, each participating to the protection of the HS within the pellets. This preservation might be due to a combination of several factors such as the early formation of pellet limiting the exchanges with the external medium and the incorporation of reduced S in the organic matter, thus increasing its stability.

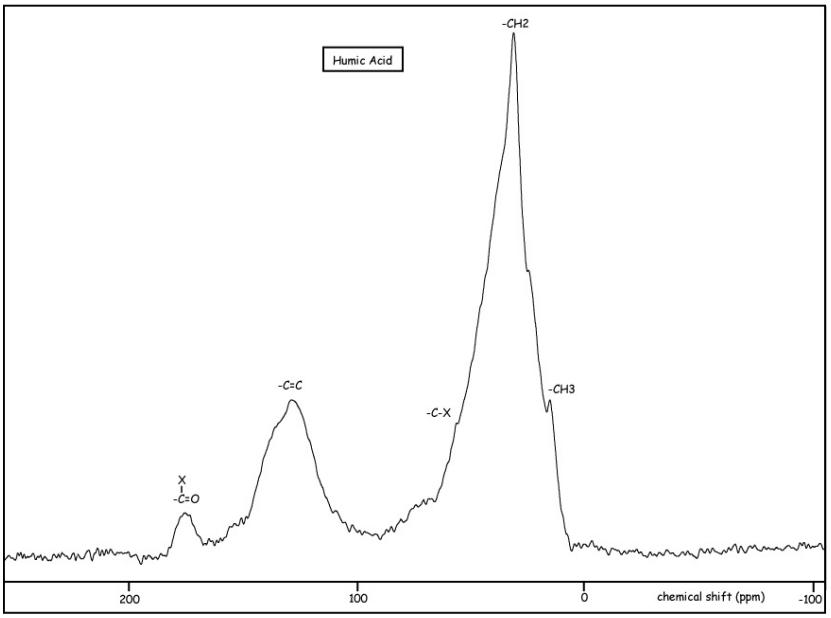

Figure 1: ^{13}C solid state NMR spectrum of a HA extracted from phosphatic “pellets” collected from Gafsa Basin phosphatic sediments

REFERENCES

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